

For publication in an unspecified foreign journal

A "CONTACT RULE" FOR RIGID-SPHERE MODELS OF CRYSTAL STRUCTURES

6p
Paul J. Shlichta [1961] 6p *refe Abstract in*
Jet Propulsion Laboratory
California Institute of Technology
Pasadena, California, U. S. A.*

X 64 10350
N65-88958
Code 2A

~~ENGLISH and GERMAN~~ Submitted for Publication
AUSZUG.

Wenn eine Kristallstruktur als eine Raumgruppenanordnung sich berührender, fester Kugeln betrachtet wird, dann gilt das Verhältnis $F = P - C + 1$, worin "P" die Anzahl der veränderlichen Parameter der Struktur ist und "F" die Freiheitsgrade im Parameter-Raum, wenn "C" Berührungsweisen vorhanden sind. Diese "Kontaktregel" ist analog zu Gibbs' "Phasenregel" und kann auf ähnliche Weise angewendet werden, wie z.B. zur Konstruktion von "Kontakt-Diagrammen". Diese sind zur optimalen Bestimmung von Atompositions-Parametern, zur Zuordnung folgerichtiger Werte für Atomradien und zur Charakterisierung der Bindungsart nützlich.

ABSTRACT

10350

If a crystal structure is regarded as a space-group array of rigid spheres in contact, then the relationship $F = P - C + 1$ holds, where P is the number of variable parameters of the structure and F is the number of degrees of freedom in parameter-space when C modes of contact are achieved. This "Contact Rule" is analagous to Gibbs' Phase Rule and may be applied in similar ways such as the construction of "contact diagrams". These are useful for optimizing atomic position parameters, for deriving consistent values for atomic radii, and for characterizing bond type.

Author

A crystal structure may be treated as a space-group array of rigid spheres in contact; this premise underlies all usage of atomic radii. According to this approximation, the number of contacts in a given structure is useful as a qualitative index of its stability and bonding energy. Unfortunately, most structures have a large number of variable parameters -- the (n-1) radius ratios of the n atomic species, the space-group position parameters, and the unit cell axial ratios and/or angles -- so that a trial-and-error calculation of all possible contacts

*The work described herein represents one phase of research sponsored by the National Aeronautics and Space Administration under Contract NAS 7-100

(NASA CR-52613)

Available to NASA Offices and
NASA Centers Only.

Article 10000 Offices and
WASH Centers Only

throughout parameter-space is impractical. It can be shown, however, that there exists a simple topological relation which determines the maximum number of contact modes (i.e., classes of symmetry-equivalent contacts) for any given structure.

A crystal structure, expanded so that none of its atoms are in contact, has a degree of freedom (i.e. an arbitrary variable) corresponding to each of its variable parameters, plus an additional one corresponding to the implicit variable of unit-cell expansion (i.e. a_0 / R_1). Let us assume that the structure then contracts until some of the atoms come into contact. Each mode of contact specifies a parameter or a relationship between parameters and therefore eliminates one of the degrees of freedom. Hence, for any crystal structure,

$$F = P - C + 1$$

where F is the number of degrees of freedom, P is the number of variable parameters, and C the number of contact modes. This equation is identical in form to Gibbs' Phase Rule and has a comparable variety of applications.

The sodium chloride structure provides a simple illustration. It has only one variable parameter (P), the anion-cation radius ratio, but there are three possible contact modes (C); anion-anion along $\langle 110 \rangle$, cation-cation along $\langle 110 \rangle$, and anion-cation along $\langle 100 \rangle$. According to the "contact rule", stated above;

1. one contact mode permits one degree of freedom;
e.g. anion-cation contact is possible for any radius ratio between 0.414 and 2.413;
2. two contact modes permit no degrees of freedom, so that the structure is completely specified; e.g. simultaneous anion-anion and anion-cation contact fix the anion-cation radius ratio at 2.413;

3. It is impossible to achieve all three contact modes simultaneously.

These conclusions may be verified by geometric construction.

For a structure with two variable parameters, it is necessary to construct a "contact diagram", similar in many respects to a phase diagram. Figure 1 shows the contact diagram for the hexagonal AlB_2 (C32) structure (Figure 2). Each area defines the field of a single contact mode, each boundary line defines the conditions for achieving two contact modes simultaneously, and each point of intersection specified the parameters which permit three simultaneous contact modes.

Connectivity - the incorporation of all the atoms in the lattice into one continuous contact-network - is a plausible requirement of any real crystal structure, although apparent exceptions, such as lithium iodide, do exist. Since connectivity depends qualitatively on the number and types of contact modes, the regions of connectivity in a contact diagram correspond to entire contact-mode fields and/or the boundaries between them; these may be designated by shaded areas and solid boundaries. In the AlB_2 structure, for example, XY contact is both a necessary and a sufficient condition for connectivity (See Figure 1).

When applied to specific structures, contact diagrams may be used to determine bond type and to derive empirical atomic radii. Ideal metallic or ionic bonding may be validly approximated by rigid spheres in contact; hence the contact rule and the requirement of connectivity should normally apply. Therefore, for a metallic AlB_2 structure, for which it may plausibly be assumed that maximum packing

fraction and hence maximum contact is desirable*, the triple points at the corners of the XY field would seem to be best. On the other hand, for an ionic structure one wishes to maximize anion-cation contacts while minimizing contacts of like ions; this would be realized near the center of the XY field. Covalent bonding, however, is highly directional and permits a continuous range of bond distances, with no specifiable "contact distance". Therefore neither the concept of atomic radii nor the contact rule applies to covalent structures, and these cannot be assigned to any specific position on a contact diagram.

These criteria may be illustrated by typical AlB_2 -type structures. The rare earth gallium compounds - $CeGa_2$, $LaGa_2$, etc. - all have a c_0 / a_0 axial ratio of approximately 1.0 (Haszko, 1961). Assuming conventional metallic radii (Pauling, 1947) these structures would lie deep in the nonconnective region of the YYb field of the AlB_2 contact diagram; this suggests that these structures are not ideally metallic. If we assume some degree of ionic character, the gallium having a partial positive charge, the radius ratio R_x/R_y would increase and the position of these structures on the contact diagram would shift toward the center of the XY field, a location consistent with the postulate of ionic character. In contrast, the transition metal borides, such as ZrB_2 and WB_2 have c_0 / a_0 axial ratios greater than 1.1 (Brewer et al., 1951), so that it is impossible to place these structures on a connective portion of the AlB_2 contact diagram. Therefore these structures are probably predominantly covalent.

*

Throughout the nonconnective regions of a contact diagram, the points of maximum contact correspond to packing-fraction maxima; this is not necessarily true, however, within the connective regions.

Numerous other applications of the contact rule are possible, including a mathematical treatment for structures having more than two parameters. A detailed exposition is in preparation and will be published elsewhere. It should be borne in mind, however, that the contact rule is a law of geometry only, and not of chemistry or physics; it does not apply to real crystal structures, but merely to one kind of idealized model of crystal structures.

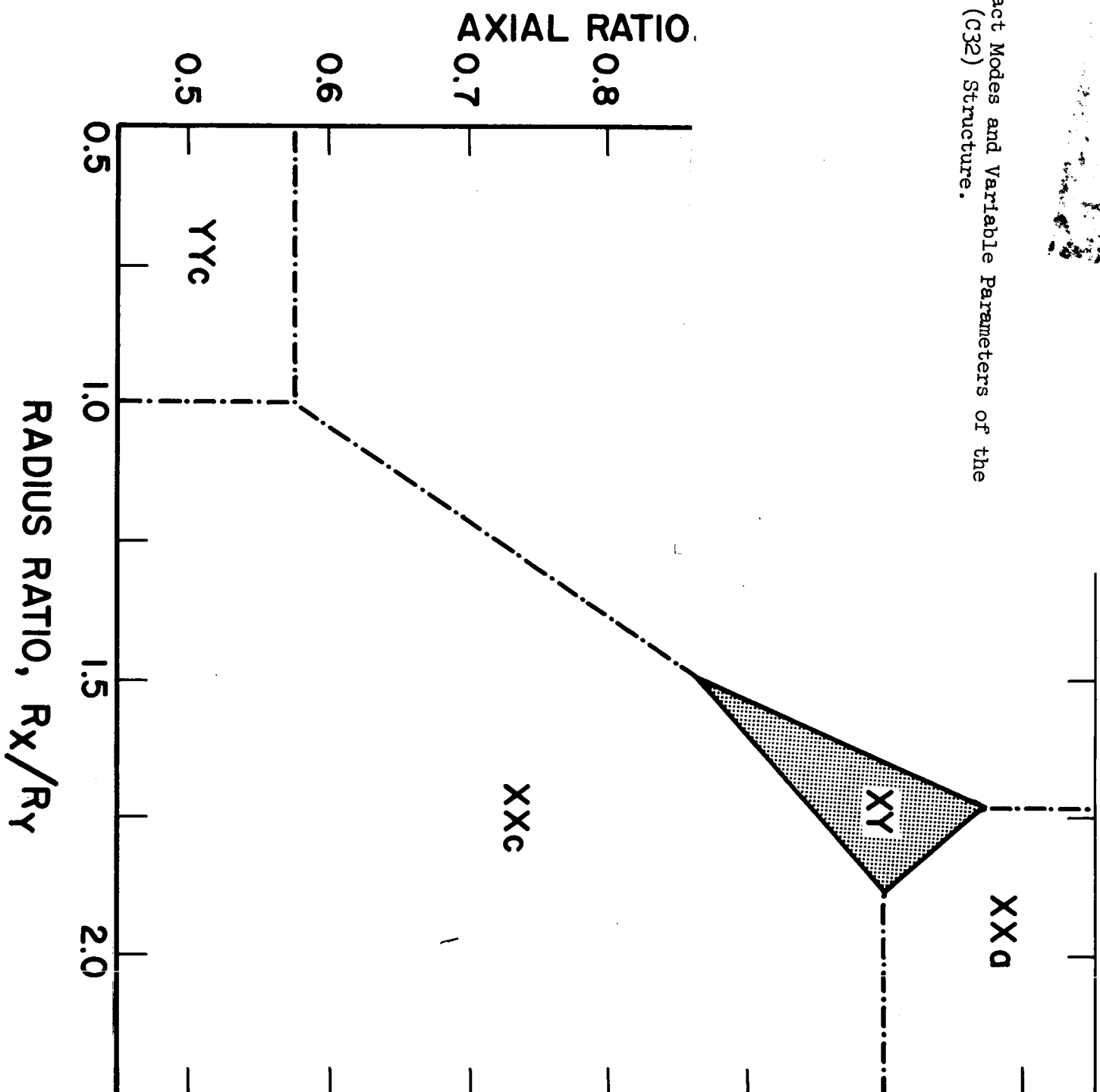
REFERENCES

- Brewer, L., Sawyer, D. L., Templeton, D. H., and Daugen, C., "A Study of the Refractory Borides" J. Amer. Ceram. Soc., 34, 173-179 (1951)
- Haszko, S. E., "Rare-Earth Gallium Compounds Having the Aluminum-Boride Structure", Trans. A.I.M.E., 221, 201-202 (1961)
- Pauling, L., "Atomic Radii and Interatomic Distances in Metals", J. Amer. Chem. Soc., 69, 542-553 (1947).

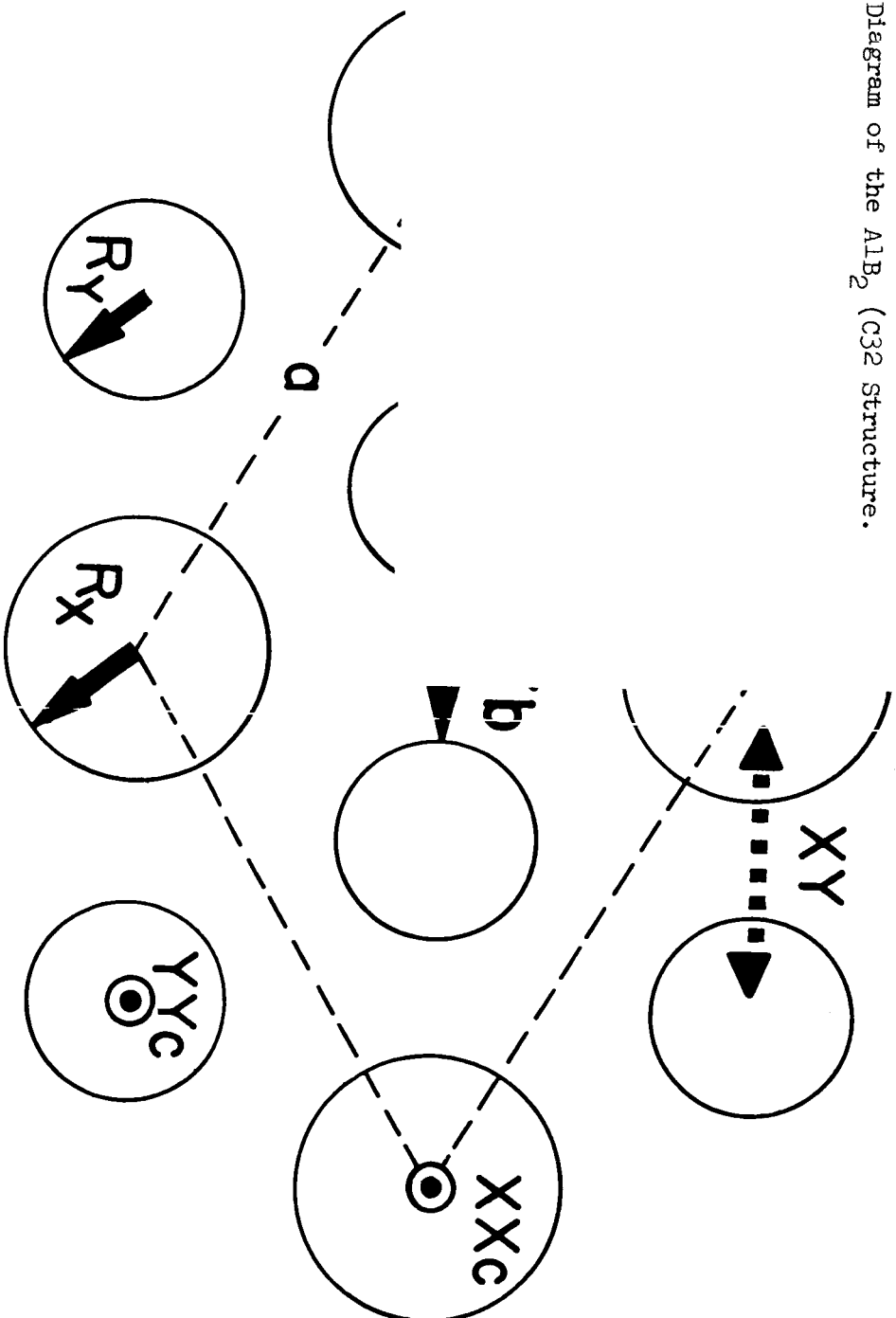
FIGURE

1. Contact Diagram of the AlB_2 (C32) Structure.
2. Contact Modes and Variable Parameters of the AlB_2 (C32) Structure.

2. Contact Modes and Variable Parameters of the
ALB₂ (C32) Structure.



1. Contact Diagram of the AlB_2 (C32 Structure).



$= X(AI),$
at $C=0$

$= Y(B),$
at $C=1/2$